

Requested Patent: GB474922A

Title: PROCESS FOR CHLORINATING AND BROMINATING HYDROCARBONS ;

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Equivalents: ;

#### ABSTRACT:

In the chlorination or bromination of saturated aliphatic hydrocarbons having 3 or more carbon atoms in the vapour phase at temperatures at which the product is separated by condensation at the instant of formation, the halogen is blown into the reaction space through one or more capillaries in counter-current to the hydrocarbon. The hydrocarbon is preferably in excess, and the reaction may be effected in the presence or absence of actinic light and under diminished or increased pressure. Hydrocarbons specified are propane, butane, isobutane, the isomeric pentanes, hexanes, heptanes, decanes, undecanes, dodecanes, or mixtures thereof. The hydrocarbon is boiled in a flask 1, the vapours passing through tube 2, column 3, and dephlegmator 4 to reaction chamber 5 where the halogen is blown in through capillary 6 against the ascending vapours. Excess hydrocarbon is condensed in condenser 7, hydrogen halide leaves by pipe 8 and the halogenation product enters flask 1 through tube 9. The capillaries preferably have a cross-sectional area not greater than about  $\frac{1}{1000}$ th of that of the reaction chamber, thus the respective diameters may be 1 mm. and 34 mm. Examples describe the chlorination of butane, heptane, dodecane, and petroleum fractions consisting chiefly of heptanes or pentanes, and the bromination of pentane to give mainly monohalogeno products.

## PATENT SPECIFICATION



Application Date: May 14, 1936. No. 13690/36.

474922

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Complete Specification Accepted: Nov. 15, 1937.

## PROVISIONAL SPECIFICATION

## Process for Chlorinating and Brominating Hydrocarbons

I, WILFRED WILLIAM GROVES, a British Subject, of 30, Southampton Buildings, London, W.C.2, do hereby declare the nature of this invention (as communicated  
5 to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, a Joint Stock Company organised according to the laws of Germany, of Frankfurt a/Main, Germany) to be as follows:—

10 In the art of halogenating organic compounds, for example hydrocarbons in the form of vapour it is the practice to condense immediately the halogenated product and thereby to withdraw it from  
15 further halogenation. Notwithstanding this the operation easily leads to the production of more highly halogenated compounds. The cause of their formation resides chiefly in the faulty intermixture  
20 of the vapour to be halogenated with the halogenating agent. This gives rise to a local high concentration and rise of temperature.

This invention is based on the observation that these difficulties may be avoided  
25 if in the chlorination or bromination of saturated or aliphatic hydrocarbons having three or more carbon atoms in the vapour phase and at a temperature at which the product of halogenation is separated from  
30 the reaction zone by condensation at the instant of its formation the operation is so conducted that the gaseous chlorine or bromine is blown in opposite direction to  
35 the hydrocarbon vapour through narrow capillaries into the reaction chamber. Advantageously the hydrocarbon to be chlorinated or brominated is heated to  
40 boiling in a flask and the reaction is carried out in a chamber superimposed on the flask. Preferably the compound to be halogenated is used in excess. Owing to the movement in opposite directions of the  
45 two components of the reaction and the speed at which the chlorine or bromine enters the zone a complete intermixture of the components is obtained extremely quickly. The halogen under these conditions reacts at once with the large excess  
50 of hydrocarbon vapour present in the chamber without profound chlorination or bromination occurring.

The liberated heat of reaction can be

removed by sprinkling the wall of the reaction chamber with the excess of hydro- 55 carbon which has been condensed in a condenser arranged above the chamber.

When the process is complete the excess of hydrocarbon is distilled from the flask and the residual alkyl chloride or bromide 60 is purified by distillation.

Obviously the halogenation may be assisted by the presence or absence of actinic light and the process may be conducted under diminished or increased 65 pressure. The method may be applied both to pure hydrocarbons and to mixtures of hydrocarbons.

The following examples illustrate the invention:—

1. 100 kilos of heptane are heated to 70 boiling. The vapour passes through a column into the reaction chamber where the chlorine gas is blown through capillaries into the oppositely streaming 75 vapour. The heptyl chloride thus produced is immediately condensed and flows together with the excess of heptane which has been condensed by a condenser arranged above the chamber, through the 80 column into the boiling flask. The process is interrupted when the greater part of the heptane has been converted into the chloride. The excess of hydrocarbon is then distilled. The heptyl chloride re- 85 maining in the flask is then purified by distillation. It boils at 143—144° C. The yield of pure monochlorheptane amounts to 96 per cent of the chlorinated product. 90

2. Pentane is boiled and the vapour rising through the column is met in the reaction chamber by a counter-blast of gaseous bromine introduced through a narrow capillary. Otherwise the mode of 95 operation is similar to that described in Example 1. The yield of monobrominated pentane amounts to 94—96 per cent.

3. Butane is boiled as described in Example 1 and chlorine gas is blown 100 through capillaries in opposite direction into the rising stream of butane vapour. Chlorination proceeds smoothly at 10—20° C. Advantageously the reaction chamber may be illuminated. The condenser 105 placed above the reaction chamber may be

fed with cold lye. When the greater part of the butane has been chlorinated the unchanged hydrocarbon and afterwards the butyl chloride is distilled. The yield of

the monochloro product is 93 per cent.

Dated this 14th day of May, 1936.

ABEL & IMRAY,

Agents for the Applicant.

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### COMPLETE SPECIFICATION

#### Process for Chlorinating and Brominating Hydrocarbons

I, WILFRED WILLIAM GROVES, a British Subject, of 30, Southampton Buildings, London, W.C.2, do hereby declare the nature of this invention (as communicated  
10 to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, a Joint Stock Company organised according to the laws of Germany, of Frankfurt a/Main, Germany) and in what manner the same is to  
15 be performed, to be particularly described and ascertained in and by the following statement:—

In the art of halogenating organic compounds, for example hydrocarbons, in the  
20 form of vapour it is the practice to condense immediately the halogenated product and thereby to withdraw it from further halogenation. Notwithstanding this the operation easily leads to the pro-  
25 duction of more highly halogenated compounds. The cause of their formation resides chiefly in the faulty intermixture of the vapour to be halogenated with the halogenating agent. This gives rise to a  
30 local high concentration and rise of temperature. Even when, as has already been proposed, the halogen is introduced through fine perforations or small tubes or nozzles, it is not possible to suppress  
35 adequately the formation of more highly halogenated compounds.

This invention is based on the observation that these difficulties may be avoided if in the chlorination or bromination of  
40 saturated, aliphatic hydrocarbons having three or more carbon atoms in the vapour phase and at a temperature at which the product of halogenation is separated from the reaction zone by condensation at the  
45 instant of its formation, the operation is so conducted that the gaseous chlorine or bromine is blown into the reaction chamber through one or more narrow capillaries in opposite direction to the  
50 hydrocarbon vapour. Preferably a single capillary is used. Advantageously the hydrocarbon to be chlorinated or brominated is heated to boiling in a flask and the reaction is carried out in a chamber which  
55 is superimposed on the flask and wherein the temperature is adjusted so that it is below the boiling point of the products of halogenation which are formed. Preferably the compound to be halogenated  
60 is used in excess. Owing to the movement of the two components of the reaction in

opposite directions and the speed at which the chlorine or bromine enters the zone a complete intermixture of the components is obtained extremely quickly. The  
65 halogen under these conditions reacts at once with the large excess of hydrocarbon vapour present in the chamber without profound chlorination or bromination occurring.

The liberated heat of reaction can be removed by sprinkling the wall of the reaction chamber with the excess of hydrocarbon which has been condensed in a  
70 condenser arranged above the chamber.

When the process is complete the excess of hydrocarbon is distilled from the flask and the residual alkyl chloride or bromide is purified by distillation.

Obviously the halogenation may be  
80 assisted by the presence or absence of actinic light and the process may be conducted under diminished or increased pressure. The method may be applied both to pure hydrocarbons and to mixtures  
85 of hydrocarbons.

The process may, for instance, be performed in the apparatus illustrated by way of example in the accompanying  
90 drawing.

The substance to be halogenated is heated to boiling in the flask 1. The vapours pass through the tube 2, the column 3 and the dephlegmator 4 into the reaction chamber 5, where the gaseous  
95 halogen is blown in through the capillary 6 arranged in a direction opposite to that of the vapours. Above the reaction chamber 5 is the condenser 7, which retains an excess of the parent  
100 material to be chlorinated, and the exit pipe 8 for the hydrogen halide produced. The product of halogenation thus formed enters the flask 1 through the tube 9.

As capillaries there are preferably used  
105 tubes having a cross-sectional area not greater than about 1/1000 of the area of the cross-section of the outer tube (reaction chamber). It has been possible to obtain very good results with the aid of  
110 an apparatus in which capillaries have a diameter of 1 mm. and the reaction chamber a diameter of 34 mm. In practice, however, the operation is best conducted with a ratio of the areas of the cross-  
115 sections of about 1 to 10000 to 1 to 30000. The ratio may also be as low as about 1

to 100,000, that is to say, the capillaries may have a diameter of 1 mm. and the reaction chamber may have a diameter of about 34 cm.

5 As parent materials for the process there may be used for instance propane, butane, isobutane, *n*-pentane and the isomers thereof, *n*-hexane and the isomers thereof, the isomeric heptanes, furthermore hydrocarbons of high molecular weight such as decane, undecane and dodecane as well as the isomers thereof. Especially mixtures of the isomers or mixtures of hydrocarbons containing different numbers of carbon atoms may be halogenated.

10 The following Examples illustrate the invention:—

1. 100 kilos of heptane are heated to boiling. The vapour passes through a column into the reaction chamber where the chlorine gas is blown through a capillary into the oppositely streaming vapour, the ratio of the diameter of the capillary to the diameter of the reaction chamber being 1:150. The heptyl chloride thus produced is immediately condensed and flows together with the excess of heptane which has been condensed by a condenser arranged above the chamber, through the column into the boiling flask. The process is interrupted when the greater part of the heptane has been converted into the chloride. The excess of hydrocarbon is then distilled. The heptyl chloride remaining in the flask is then purified by distillation. It boils at 143—144° C. The yield of pure monochloroheptane amounts to 96 per cent. of the chlorinated product.

2. Pentane is boiled and the vapour rising through the column is met in the reaction chamber by a counter-blast of gaseous bromine introduced through a narrow capillary, the ratio of the diameter of which to the diameter of the reaction chamber is 1:300. Otherwise the mode of operation is similar to that described in Example 1. The yield of monobrominated pentane amounts to 94 to 96 per cent.

3. Butane is boiled as described in Example 1 and chlorine gas is blown through a capillary in opposite direction into the rising stream of butane vapour, the ratio of the diameter of the capillary to the diameter of the reaction chamber being 1:150. Chlorination proceeds smoothly at 10—20° C. Advantageously the reaction chamber may be illuminated. The condenser placed above the reaction chamber may be fed with cold lye. When the greater part of the butane has been chlorinated the unchanged hydrocarbon and afterwards the butyl chloride is distilled. The yield of the monochloro product is 93 per cent.

4. 100 kilos of a fraction of petroleum which boils at about 100—125° C. and consists chiefly of a mixture of heptanes are heated to boiling in a still. The vapour passes through a column and then enters the reaction chamber, into which chlorine gas is blown through a capillary in opposite direction to the vapour, the ratio of the diameter of the capillary to the diameter of the reaction chamber being 1:150. The monochloride thus produced is immediately condensed and flows through the column into the still together with the excess of hydrocarbon which has been condensed in a condenser arranged above the reaction chamber. The process is interrupted when most of the starting material has been converted into the chloride. The excess of unchlorinated hydrocarbons is then distilled. In the flask there remains a mixture of heptyl monochlorides which boils at about 142—160° C. The yield amounts to 94 per cent. of the chlorinated starting product; the remainder consists of more highly chlorinated by-products.

5. 72.1 kilos of a mixture of pentanes from a fraction of petroleum which boils between about 30° C. and about 50° C. are chlorinated as described in Example 1, except that the ratio of the diameter of the capillary to the diameter of the reaction chamber is 1:300. After the starting material which has not been halogenated is distilled a crude chlorination product is obtained of which 96 per cent. consists of a mixture of amyl monochloride which distils between about 92° C. and about 107° C. and is purified by distillation. The residue consists chiefly of dichloropentanes, together with some more highly chlorinated products.

6. Dodecane is boiled as described in Example 1 and the vapours of the hydrocarbon in the reaction chamber are chlorinated by blowing in chlorine through a capillary in opposite direction to the vapours, the ratio of the diameter of the capillary to the diameter of the reaction chamber being 1:150. The process is interrupted when most of the dodecane has been chlorinated. The unchanged starting material is then separated under reduced pressure and the pure dodecyl chloride is obtained which distils at 90—94° C. at a pressure of 10 mm. The yield of pure monochlorododecane surmounts 94 per cent. of the total chlorination products. The remainder consists of more highly chlorinated products.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim

is:—

1. A process for chlorinating or  
brominating saturated aliphatic hydro-  
carbons having three or more carbon  
5 atoms in the vapour phase and at a tem-  
perature at which the product of halogena-  
tion is separated from the reaction zone  
by condensation at the instant of its for-  
mation, wherein the gaseous chlorine or  
10 bromine is blown into the reaction space  
through one or more capillaries in counter  
current to the vapour of the hydrocarbon.

2. A process for chlorinating or

brominating saturated aliphatic hydro-  
carbons, substantially as described with 15  
reference to any one of the Examples  
herein.

3. Chlorinated and brominated satur-  
ated aliphatic hydrocarbons when pre-  
pared or produced by the process of manu- 20  
facture particularly described and ascer-  
tained herein or by any process which is  
an obvious chemical equivalent thereof.

Dated this 13th day of April, 1937.

ABEL & IMRAY,  
Agents for the Applicant.

*[This Drawing is a full-size reproduction of the Original.]*

